POLYMER CHARACTERIZATION NEWS FROM LOUGHBOROUGH UNIVERSITY

Micro-Thermal Analysis of Polymers

Thermal methods of analysis, such as Differential Scanning Calorimetry (DSC) and Thermomechanical Analysis (TMA), are widely used for the characterization of polymers. However, the results of such measurements represent the sum of all of the constituents in the sample. The bulk thermal response is often dominated by the higher concentration of the matrix or substrate material. It is difficult to gain detailed characterization of dilute components, contaminants and less dominant phases without physically altering the sample. In addition, the experiments are often time-consuming, particularly for thermomechanical tests.

Micro-Thermal Analysis (Micro-TA) combines the imaging capabilities of Atomic Force Microscopy (AFM) with the characterization capability of thermal analysis. This is the result of collaboration between Mike Reading at the Institute of Polymer Technology & Materials Engineering at Loughborough University and Hubert Pollock & Azzedine Hammiche at the School of Physics & Chemistry at Lancaster University in the United Kingdom. TA Instruments and ThermoMicroscopes have now commercialized the equipment, which has already attracted several prestigious awards.

Micro-TA uses a conventional atomic force microscope in which the conventional probe has been replaced by an ultra-miniature resistive heater/thermometer. The conventional topographic image may still be acquired but now it is possible to generate images whose contrast is determined by the thermal properties of the surface such as its apparent thermal conductivity. This is obtained from the power required to maintain the tip at a constant temperature as it is rastered over the sample. This mode is particularly useful for examining composites (Figure 1), filled materials and polymer blends (Figure 2). By imposing an AC temperature modulation on the probe, the depth of penetration of the thermal wave is dependent on its frequency. It is envisaged that this will enable a form of tomographic imaging to be carried out.

The tip, when used in conjunction with a reference probe, can be used as an ultra-miniature Differential Thermal Analyser (DTA) cell. Having imaged the sample, any point in the surface can be selected and the probe tip placed upon it. The temperature of the tip can then be changed in exactly the same way as conventional thermal analysis to obtain calorimetric measurements of transitions. In addition, the z-axis deflection of the tip can be monitored during the scan in a method closely analogous to Thermomechanical Analysis (TMA). Both the calorimetric and mechanical property measurements are made simultaneously affecting an area only a few microns square. Because of the small thermal mass of the probe, heating rates as high as 1000°C/min can be employed.

Figure 3 shows the topography of a cross section through a packaging film which contains a gas barrier layer flanked by a thin "tie" layer which bonds it to the bulk of the film. Localized DTA and TMA measurements were carried out at points on each of these regions (Figure 4). The gas barrier layer can be identified as poly(ethylene-co-vinyl alcohol) whereas the bulk film is high density polyethylene and the tie layer a low/medium density polyethylene. An image of the film post-analysis (Figure 5), shows a series of "craters", several times larger than the region measured during

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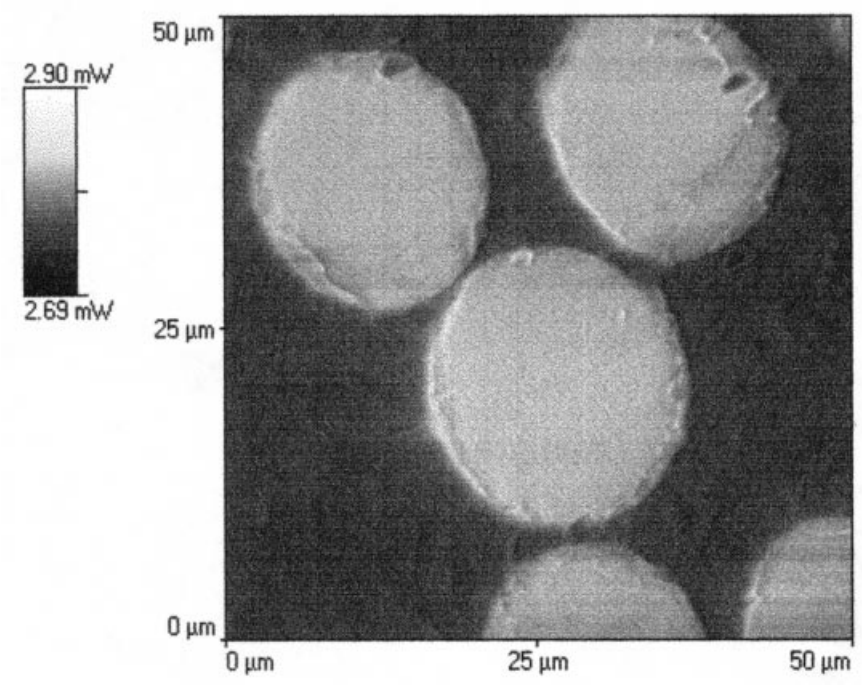

FIGURE 1. Thermal conductivity contrast image of glass fibres in a polymer matrix. The glass fibres are the bright (high thermal conductivity) circles.

tothermal IR detector or to pyrolyse specific regions for spatially-resolved evolved gas analysis.

Micro-TA provides the means to image a sample and then obtain spatially-resolved measurements on small areas thus overcoming the limitations of conventional techniques described in the opening paragraph. It also opens up a new range of applications for thermal methods in polymer science, composites, catalysis and pharmaceuticals by providing a powerful new form of analytical microscopy. An important feature of this new method is that it enables very fast experiments to be performed as, on this small scale, heating rates two orders of magnitude greater than used in conventional methods. This opens up the possibilities for rapid anal-

the test, resulting from flow of the polymer away from the hot probe as it is drawn off the sample in-between measurements.

A further example of localized thermal analysis is shown in Figure 6 where measurements were made on the high and low thermal conductivity regions of the image of the polymer blend shown in Figure 2. The glass-rubber transitions of each component are clearly resolved thus confirming the identities of the matrix (low T_g) and occluded phase (high T_g).

The equivalent of dynamic mechanical analysis has also been demonstrated by adding a force modulation to the probe during the thermal scan. In the future it will also be possible to obtain chemical information by using the thermal probe as a localized pho-

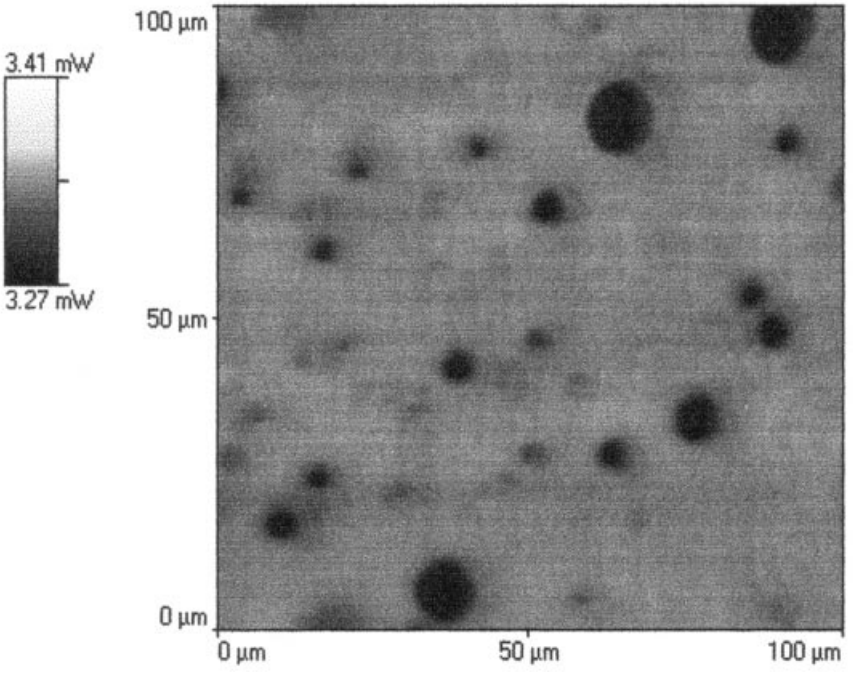

FIGURE 2. Thermal conductivity contract image of a polymer blend. The dispersed phase has lower thermal conductivity than the matrix.

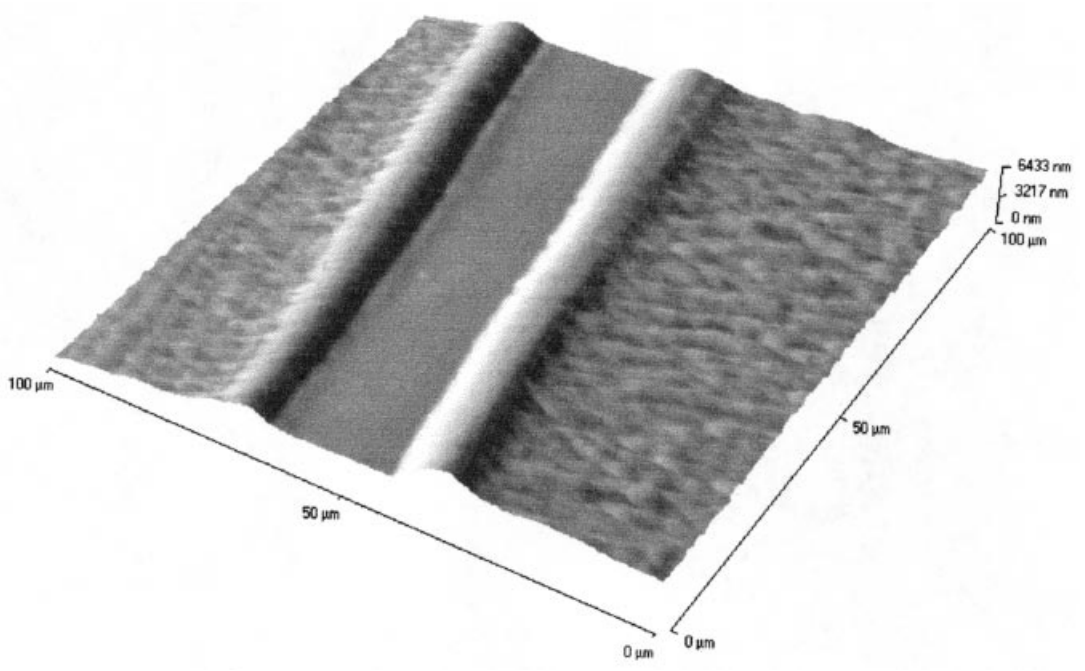

FIGURE 3. Three dimensional perspective topographic image of a cross-section through packaging film showing a central gas-barrier layer flanked by tie layers within the bulk film.

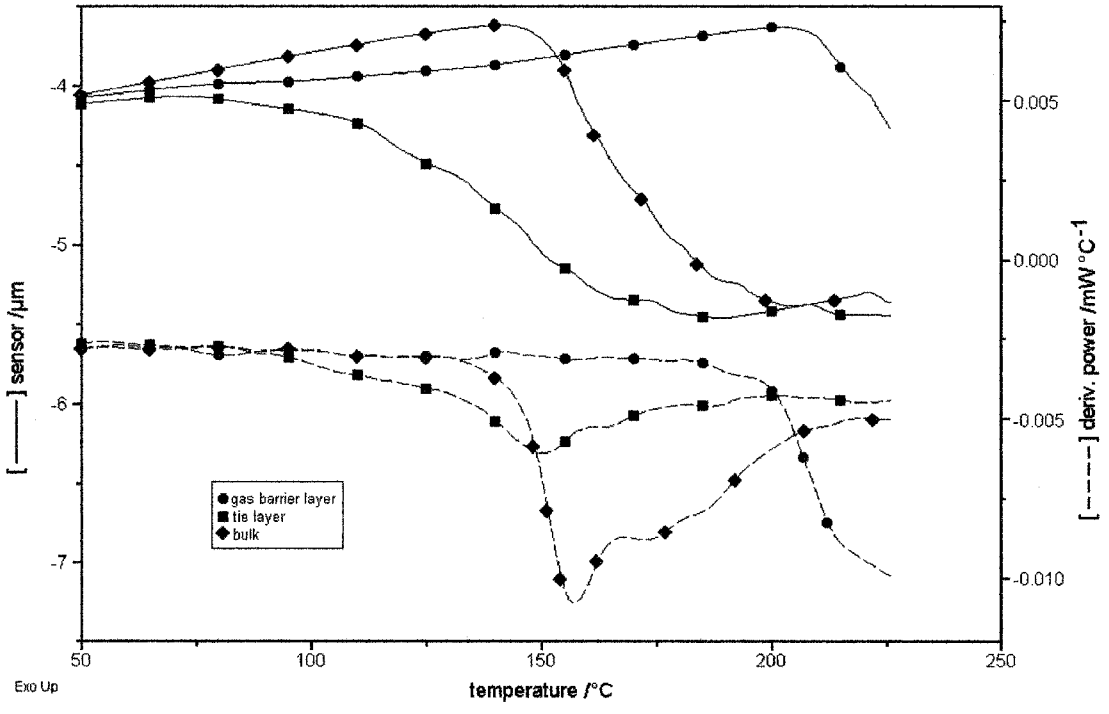

FIGURE 4. Localized thermal analysis of the gas barrier region, tie layer and bulk film.

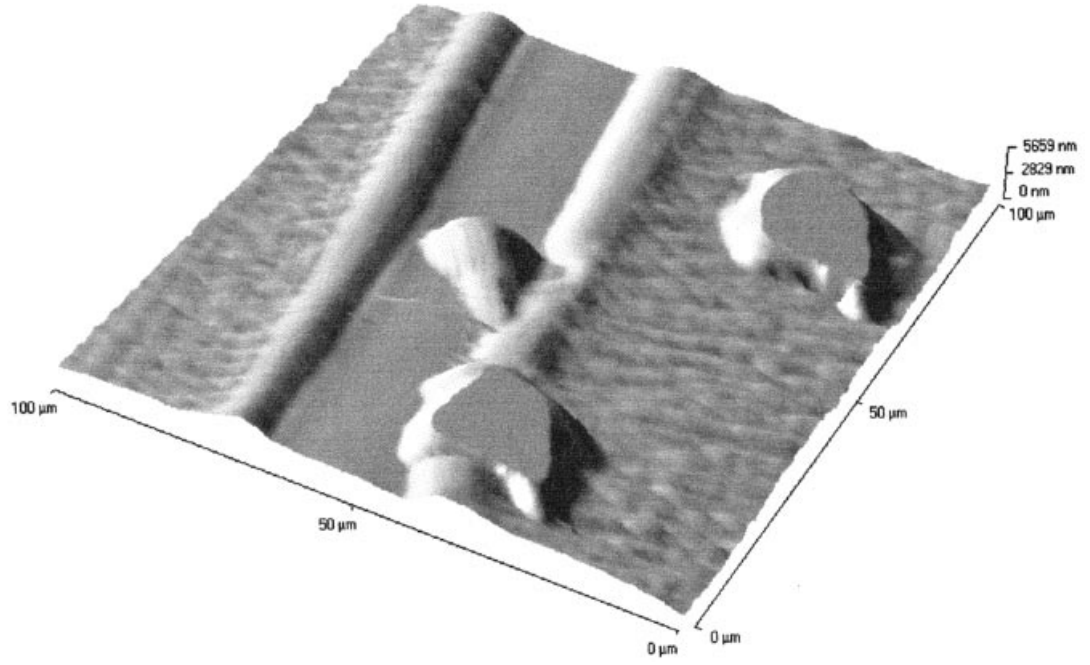

FIGURE 5. As Figure 3, following localized thermal analysis.

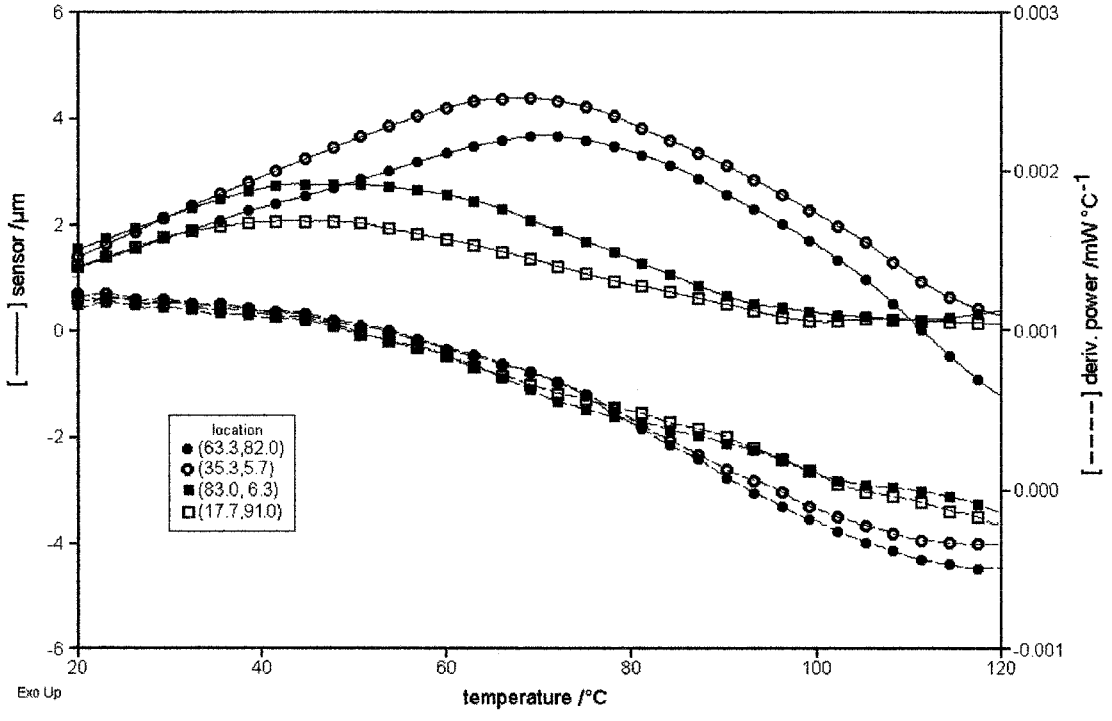

FIGURE 6. Localized thermal analysis of the blend shown in Figure 2 identifying each phase from its glass-transition (softening) temperature.

ysis of very large numbers of samples.

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Further Reading

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